

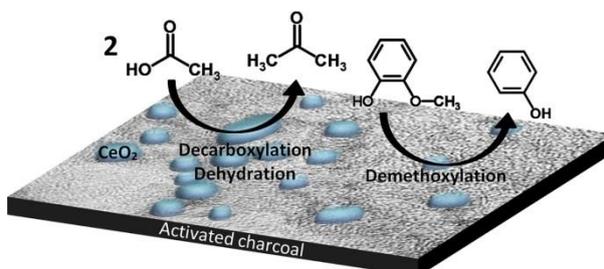
8- Materials and membranes for green fuel production

Catalytic deoxygenation of model compounds from flash pyrolysis of lignocellulosic biomass over activated charcoal based catalysts

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Collaboration : CIRAD-Montpellier- France, 2IE-Ouagadougou- Burkina Faso, IRCELyon- Villeurbanne-France
Involved MCP researcher: Anne Julbe

Catalytic deoxygenation of pyrolytic vapors represents a great challenge to produce biofuels by flash pyrolysis of lignocellulosic biomass. A wide variety of catalysts, particularly zeolites, have been investigated for this purpose, however, quick deactivation was often reported. Although they are cheap and can have a hierarchical pore structure, activated charcoal-based catalysts have received only little attention. This paper presents an innovative method to synthesize activated charcoal based catalysts doped with CeO_2 , Fe_2O_3 or Mn_3O_4 nanoparticles. We investigated the performances of those catalysts to deoxygenate two biomass pyrolytic model compounds – acetic acid and guaiacol – on a fixed-bed reactor between 350 °C and 450 °C. Ceria-based catalyst was highly active and remarkably stable to enhance ketonic decarboxylation of acetic acid, leading to the formation of acetone. Huge amounts of produced phenol attest for the partial deoxygenation of guaiacol, particularly when using iron-based catalyst. This study demonstrates the potential of activated charcoal-based catalysts to produce weak-acidic and partially deoxygenated bio-oils.



Mastering the kinetics of the CO₂-char gasification through the catalyst/biomass integration concept

Fuel 154 (2015) 217–221

Collaboration: CIRAD-Montpellier- France, 2IE-Ouagadougou- Burkina Faso
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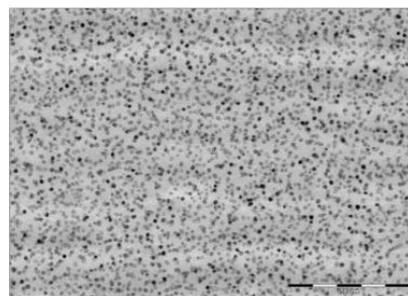
The catalyst/biomass integration concept is demonstrated to promote the reduction of char residence time and/or energy consumption through the catalysis of the rate limiting step of the whole biomass gasification process. Both the in-situ formation of the Ni^0 nano catalyst and the CO_2 gasification of the resulting nanocomposite char/nano Ni^0 can occur at temperatures as low as 500 °C.



Pyrolysis of biomass impregnated with metal nitrate salts

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Collaboration: CIRAD-Montpellier- France, 2IE-Ouagadougou- Burkina Faso
Involved MCP researcher: Anne Julbe



Catalytic pyrolysis is a promising way to improve bio-oil product quality. In this study, metal salts were directly impregnated in biomass to generate in situ catalysts and investigate their impact on pyrolysis products. Seven metals – Ce, Mn, Fe, Co, Ni, Cu and Zn – were selected and impregnated in eucalyptus using nitrate salts. A fixed-bed reactor, pre-heated at 500 °C and inerted with N₂ flow, was used for pyrolysis. Both gas and bio-oil compositions were analysed, paying particular attention to the production of anhydrosugars. The anhydrosugar yields were found to be strongly influenced by the presence of metal salt catalysts. In particular, both Zn and Co salts yielded more anhydrosugars in comparison with catalyst-free sample. Moreover, LAC (1-hydroxy-(1R)-3,6-dioxabicyclo[3.2.1]octan-2-one) was produced in higher amounts than levoglucosan which is commonly produced without any catalyst. Metals were found to remain in all chars and tended to form metal-based nanoparticles (e.g. Cu⁰, Ni⁰, ZnO) able to act as in situ catalysts during the pyrolysis process. It seems that those metal nanoparticles are closely related to LAC production. In parallel to metal cations, nitrates were also suspected to play a significant role during pyrolysis. The suspected impact of anions on levoglucosenone production is discussed. Concerning gas yields, the impregnated nitrate salts were found to strongly affect CO₂ production.

TEM observation of Ni-based nanoparticles in char derived from biomass pyrolysis at 500 °C (full scale bar: 200 nm).

Demonstration of a ceria membrane solar reactor promoted by dual perovskite coatings for continuous and isothermal redox splitting of CO₂ and H₂O

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CO₂ single-step thermolysis was achieved using oxygen permeable MIEC (mixed ionic-electronic conducting) membranes made of ceria for separate production of CO on the feed side and O₂ on the sweep side. The CO₂-dissociation reaction was driven by concentrated solar energy as a renewable thermal energy source and by applying a chemical potential gradient between both membrane sides. A continuous oxygen transfer across the membrane was achieved thanks to a flow of inert gas on the permeate side. This created the required oxygen partial pressure gradient and favored oxygen permeation via oxygen ion diffusion through the ceria membrane thickness. A novel solar chemical reactor integrating the reactive ceria membrane was designed and tested under real concentrated solar radiation, with operating temperatures up to 1550°C. The reactive part of the tubular redox membrane was located inside a well-insulated cavity receiver for homogeneous heating, which was fed with a carrier argon flow on the sweep side to facilitate the transport and removal of the permeated oxygen. The dynamic response of the solar fuel production upon changing the operating conditions (temperature, CO₂ mole fraction, and feed gas flow rate) in the membrane reactor was investigated by quantifying the evolved gas production rates. Continuous CO₂ dissociation was achieved on the feed side inside the tubular membrane with in-situ spatial separation of O₂ and CO streams across the membrane. Reliable solar membrane reactor operation under real concentrated sunlight was successfully demonstrated for the first time with stable and unprecedented CO production rates up to 0.071 μmol/cm²/s at 1550°C and CO/O₂ ratio of 2.

